FIRE RETARDANT COMPOSITIONS WITH REDUCED ALUMINUM CORROSIVITY

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of U.S. Patent Application Serial Number 09/723,567, filed November 28, 2000, which is hereby incorporated by reference in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

Not applicable.

FIELD OF THE INVENTION

The present invention relates to corrosion-inhibited fire retardant compositions. More specifically, the invention is directed to ammonium polyphosphate concentrates and other solutions containing suspended and/or soluble iron compounds and at least one biopolymer.

BACKGROUND

Aerial application of fire-retardant compositions to combat the spread of wildland fires is common. The composition of fire retardants concentrates designed for managing and controlling wildland fires are of two generally types, those which, when mixed or diluted with water to end-use concentration, result in either a gum thickened solution, and those which do not contain a gum thickener and, consequently, result in water-like solutions, which are not rheologically modified. These water-like retardant solutions exhibit inferior drop characteristics. The former may be supplied as dry powders or as suspensions or slurries generally referred to as fluids. Those concentrates that result in water-like solutions when diluted with water may contain suspended components, as well, but are generally referred to as liquid concentrates. Fire retardant

concentrates that are supplied as fluids or liquids are preferred by some because they can be simply and easily diluted to end-use strength with little mixing hardware and manpower.

Ammonium polyphosphate liquids have been used as aerially applied fire-retardants. These liquids have certain advantages in comparison to other fire-suppressing compositions since they can be transported and stored prior to use in the liquid form rather than being mixed from dry ingredients. However, concentrated liquid fire retardants and solutions prepared therefrom are extremely corrosive to aluminum and brass and mildly corrosive to other materials of construction used in handling, storage and application equipment. As used herein, all metals include alloys thereof. Accordingly, aluminum includes aluminum 2024T3, 6061 and 7074, steel includes 1010 and 4130 steel and brass includes yellow and naval brass. Since wildland fire retardants are most frequently transported to the fire and applied aerially, it is imperative that corrosive damage to the materials of construction of fixed-wing aircraft and helicopters be minimized.

Accordingly, the United States Department of Agriculture ("USDA") Forest Service has established, in "Specification 5100-304b (January 2000) Superseding Specification 5100-00304a (February 1986)," entitled "Specification for Long Term Retardant, Wildland Fire, Aircraft or Ground Application" (hereinafter, "Forest Service Specifications"), hereby incorporated by reference in its entirety, maximum allowable corrosion rates for 2024T3 aluminum, 4130 steel, yellow brass and Az-31-B magnesium. For example, the corrosivity of forest fire retardants, in concentrate, to aluminum, steel and yellow brass must not exceed 5.0 milli-inches ("mils") per year as determined by the "Uniform

Corrosion" test set forth in Section 4.3.5.1 of the aforementioned USDA, Forest Service Specifications. If the product is applied from fixed-tank equipped helicopters, the corrosivity of the fire retardants to magnesium must not exceed 5.0 mils per year. The Forest Service Specifications identify the maximum amount of corrosion acceptable when both the retardant concentrate and its diluted solutions are exposed to each metal indicated above at temperatures of 70° Fahrenheit ("F") and 120°F in both totally and partially immersed configurations. The maximum allowable corrosivity of aerially applied fire retardant diluted solutions to aluminum is 2.0 mils per year ("mpy"), and the maximum corrosivity to brass and steel is 5.0 mpy when partially immersed, and 2.0 mpy when tested in the partially immersed condition. In the partially immersed configuration, one-half of the coupon is within the solution and one-half is exposed to the vapors in the air space over the solution.

In an effort to address the corrosivity problems encountered with the use of fertilizer grade ammonium polyphosphates, sodium ferrocyanide was incorporated into the corrosive compositions. Sodium ferrocyanide has proven to be an effective corrosion inhibitor in fire retardant compositions containing ammonium polyphosphate fertilizer solutions. However, while sodium ferrocyanide is effective as a corrosion inhibitor, several disadvantages of its use make its incorporation in wildland fire retardant compositions undesirable. Specifically, the environmental and toxicological safety of ferro(i)cyanides is, at best, questionable. When exposed to acidic conditions and/or ultraviolet radiation from natural sunlight, the ferro(i)cyanide radical readily degrades releasing free iron and cyanide and/or hydrogen cyanide, which are toxic to humans, animals and aquatic life. Further, free iron emanating either from

decomposition of a portion of the ferro(i)cyanide radical, or introduced from other components or impurities within the composition, will subsequently react with remaining non-decomposed ferro(i)cyanide to form ferrous ferricyanide ("Turnbull's Blue") or ferric ferrocyanide ("Prussian Blue"), which emit a persistent blue-black or indigo-blue coloration, staining all that they contact. Consequently, neither ferricyanide nor ferrocyanide can be used in fire-retardants that are expected to fade and become non-visible over time, for example, in fugitive retardant compositions.

The magnitude of the above concerns is increased since wildland fire retardants are generally applied aerially in a less than completely controlled manner. Due to the presence of variables such as vegetative cover, smoke, or wind drift that impact the trajectory of the free-falling solution, aerially applied wildland fire retardant solutions may land on or near people, animals and in bodies of water, or on soil where it could enter the water supply.

In addition, the rheological properties of wildland fire retardant solutions during periods of extreme and relaxed shear, and its elasticity are recognized as important properties. The rheological properties of forest and brush land fire retardant solutions are important because they significantly affect the performance of the retardant during and following aerial discharge and subsequent distribution within the fuel ladder. The degree of dispersion, integrity of the retardant cloud, magnitude of wind-induced drift, as well as the continuity of coverage, retention on and penetration of the fuel complex are among those performance-related characteristics impacted. Fire retardant solutions, which exhibit increased viscosity and elastic properties, are more desired because they

are less affected by the extreme forces encountered in aerial application, e.g. wind effects, gravity, and shear force due to forward momentum.

Historically, wildland fire retardant solutions, as prepared for application, have been of three general rheological types: (1) unthickened liquid fertilizer solutions with little effective viscosity and elasticity; (2) clay thickened aqueous ammonium sulfate solutions with high apparent viscosity, but little effective viscosity and no elasticity; and (3) high viscosity, pseudoplastic and elastic, gum thickened ammonium phosphate and/or sulfate solutions, which maintain an increased viscosity level and elastic character even when subjected to great amounts of shear.

Guar gums, natural polysaccharides that are extracted from the guar bean, have been used in aerially applied fire retardant to enhance the rheological properties of the retardant solutions. Guar gum thickeners function in an acceptable manner when the ammonium polyphosphate based fire retardant composition is diluted relatively soon after preparation. The rate of degradation of the guar gum thickener varies with the composition of the fertilizer grade ammonium polyphosphate and can be as short as a few hours to one week. However, when the concentrated retardant is stored for more than about one week, the rate of viscosity decreases to an unacceptable level. For example, experiments have shown that a fire retardant concentrate stored for one month prior to dilution shows little tendency to increase in viscosity for several hours and does not reach its expected viscosity level for perhaps a week. Since wildland fires occur on a non-predictable basis and a rapid response is required to treat them, this type of behavior is unacceptable.

Conventional xanthan biopolymers thickeners having particle sizes in excess of about 100 microns have also been used to alter the rheological characteristics of aerially applied fire retardants. Conventional commercially available xanthan biopolymers include but are not limited to Kelzan® and Kelzan S® from CP Kelco, Wilmington, DE, and Xanthan AC® from Jungbunzlauer International AG, Basel, Switzerland. However, like guar gums, conventional xanthan biopolymer thickeners perform unacceptably in liquid ammonium polyphosphate compositions. Even when prepared freshly, ammonium polyphosphate fire retardant concentrates containing these conventional xanthan biopolymers have a decreased ability to increase the viscosity of the solution in a timely manner, upon subsequent dilution with water. As such, the use of conventional xanthan biopolymer thickeners to improve the rheological characteristics of ammonium polyphosphate based fire retardant compositions for aerially application is less desired.

Accordingly, there is a need to provide safe and acceptable wildland fire retardants for the suppression or management of wildland fires that are not corrosive to the equipment associated with the transportation, handling and application of the retardant, have favorable rheological and aerial application characteristics and are environmentally and toxicologically friendly, thereby avoiding the above disadvantages.

SUMMARY OF THE INVENTION

In overcoming the above disadvantages, it is an object of the invention to produce a wildland fire retardant composition that has a reduced-tendency to corrode various metals, favorable rheological and aerial application characteristics, and is not negatively affected by exposure to sunlight or acidic

conditions, resulting in the release of toxic by-products that could be both environmentally and toxicologically hazardous.

It is a further object of the invention to provide a fire retardant composition that is compatible with the concept of a fugitive or fading color system, able to become invisible over time with exposure to natural sunlight.

The above and other objects are met by the present invention, which provides a corrosion-inhibited fire retardant composition including at least one fire retardant composition that includes at least one ammonium polyphosphate, at least one biopolymer having a particle diameter less than about 100 microns, and a corrosion inhibiting system that includes at least one corrosion inhibiting compound selected from a group of compounds consisting of azoles, insoluble ferric pyrophosphate, soluble ferric pyrophosphate (mixture or blend of sodium citrate and insoluble ferric pyrophosphate), ferrous oxalate, ferric citrate, ferrous sulfate, ferric ammonium citrate, insoluble ferric orthophosphate, soluble ferric orthophosphate, ferric ammonium oxalate, ferric ammonium sulfate, ferric bromide, ferric sodium oxalate, ferric stearate, ferric sulfate, ferrous acetate, ferrous ammonium sulfate, ferrous bromide, ferrous gluconate, ferrous iodide, ferric acetate, ferric fluoroborate, ferric hydroxide, ferric oleate, ferrous fumarate, ferrous oxide, ferric lactate, ferric resinate, and any combination thereof; wherein the corrosion inhibiting system is present in a minor effective amount to substantially reduce the corrosiveness of the fire retardant composition.

In a second aspect, the present invention provides a method of preparing the above-described corrosion-inhibited fire retardant compositions of the invention that includes the steps of forming an intermediate concentrate composition suitable for transportation and storage that includes the above-

described corrosion-inhibited fire retardant composition of the invention; wherein the corrosion inhibiting system is present in a minor amount effective to substantially reduce the corrosivity of the fire retardant composition of the invention and diluting the intermediate concentrate with water to form the corrosion-inhibited fire retardant compositions of the invention.

In yet a third aspect, the present invention provides a method of suppressing wildland fires that includes aerially applying to wildland vegetation, ahead of wildland fire, a fire suppressing composition that is comprised of water and the above-described corrosion-inhibited fire-retardant compositions of the invention.

In a fourth aspect, the present invention provides a method of inhibiting corrosion that includes providing a corrodible material and contacting it with an effective amount of the above-described corrosion inhibiting system of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Not applicable.

DESCRIPTION OF THE INVENTION

In accordance with the present invention, it has been discovered that a fire-retardant composition can be prepared that has a reduced tendency to corrode various metals, including aluminum, that is superior to known fire retardants in rheological aerial application characteristics and is toxicologically and environmentally safe. The corrosion-inhibited fire retardants of the invention include at least one fire retardant composition comprised of at least one ammonium polyphosphate and a corrosion inhibiting system comprised of at least one corrosion inhibiting compound selected from a group of corrosion

inhibiting compounds consisting of azoles, insoluble ferric pyrophosphate, soluble ferric pyrophosphate, ferrous oxalate, ferric citrate, ferrous sulfate, ferric ammonium citrate, insoluble ferric orthophosphate, soluble ferric orthophosphate, ferric ammonium oxalate, ferric ammonium sulfate, ferric bromide, ferric sodium oxalate, ferric stearate, ferric sulfate, ferrous acetate, ferrous ammonium sulfate, ferrous bromide, ferrous gluconate, ferrous iodide, ferric acetate, ferric fluoroborate, ferric hydroxide, insoluble ferric oleate, ferrous fumarate, ferrous oxide, ferric lactate, ferric resinate, and any combination thereof. Generally, the corrosion inhibiting system is present in a minor amount effective to substantially reduce the corrosiveness of the fire retardant composition.

In one embodiment of the invention, a small amount of at least one biopolymer is added to the fire retardant compositions of the invention. When small amounts of biopolymers are added to the fire retardant compositions of the invention, further reduction in aluminum corrosivity is experienced. As shown in Tables 7a and 7b below, the corrosion-inhibited fire retardant compositions of the invention containing biopolymers pass the corrosion requirements in both concentrate and diluted solutions. Generally, the fire retardant compositions of the invention, in concentrate, comprise in the range of about .01% to about 5.0% biopolymer. However, as one skilled in the art will appreciate, compositions comprising biopolymer concentrations outside of this range are also effective. Further, biopolymers having particle diameters outside of the above range may be incorporated into the compositions of the invention without departing from the spirit and scope of the invention. For example, fire retardant compositions containing biopolymers having particle sizes greater than about 100 microns in

combination with biopolymers having particle sizes less than about 100 microns would be obvious to one skilled in the art.

In one specific embodiment of the invention, the concentrated fire retardant composition comprises about 1.0% biopolymer. In another specific embodiment of the invention, the concentrated fire retardant composition comprises about 3.0% biopolymer.

The biopolymer may be any biopolymer having a particle size less than about 100 microns. Biopolymers suitable for use in the present invention include, but are not limited to rhamsan, xanthan and welan biopolymers having an average particle diameter less than about 100 microns. Conventional xanthan thickeners having average particle diameters in excess of about 100 microns perform unacceptably in contact with liquid ammonium polyphosphate compositions. However, the inventors have found that reducing the particle diameter of biopolymers improves the ability of the biopolymers to rapidly increase the viscosity of the fire retardant composition upon subsequent dilution with water and exhibit increased corrosion inhibition, generally.

For example, a xanthan gum, with a weight average particle diameter in the range of about 100 to about 180 microns performs unacceptably in the fire retardant composition of the present invention, while a chemically identical xanthan gum with an average particle diameter in the range of about 20 to about 70 microns performs acceptably.

In one embodiment, the corrosion-inhibited fire retardant compositions of the invention include at least one xanthan biopolymer having an average particle diameter less than about 100 microns. Unlike prior art fire retardant compositions comprising guar gum thickeners and conventional xanthan

biopolymers having average particle diameters greater than about 100 microns, the rate of viscosity of the fire retardant compositions of the invention that include xanthan biopolymer show viscosity development that is unaffected by the length of time that the biopolymer is in contact with the ammonium polyphosphate fire retardant solution. Some xanthan biopolymers suitable for use in the present invention are found in Xanthan Gum-natural biopolymer for scientific water control, Fifth Edition, herein incorporated by reference in its entirety.

The corrosion-inhibited fire retardant compositions of the invention, specially adapted for aerial application to wildland fires, are prepared by forming an intermediate concentrate composition comprising the above-described fire retardant composition containing the above-described corrosion inhibiting system. The intermediate concentrate is then diluted with water to form the corrosion-inhibited fire retardant composition of the invention. Generally, the corrosion inhibiting system is present in the corrosion-inhibited fire retardant of the invention in a minor amount effective to substantially reduce the corrosiveness of the fire retardant composition.

In accordance with the present invention, the corrosion-inhibited fire retardants of the invention include a fire retardant comprised of at least one ammonium polyphosphate. Ammonium polyphosphate is also referred to as polyammonium phosphate and may include both ortho- and polyphosphate, other ammonium phosphates such as pyro- and metaphosphates, the alkali metal equivalents thereof, as well as a blend of phosphate polymers.

The ammonium polyphosphate solutions that are used as agricultural fertilizer and wildland (vegetative) fire retardants are manufactured by

neutralizing aqueous solutions of wet-process phosphoric acid, generally containing about 68% to about 74% phosphorus pentoxide with anhydrous ammonia in such a manner that both high temperature and pressure are experienced. When prepared in this manner, a portion of the impure orthophosphoric acid polymerizes or condenses, resulting in the formation of pyrophosphate, short chain polyphosphates and, in most instances, small amounts of cyclic or metaphosphates. That portion of the acid that does not polymerize, of course, remains as orthophosphoric acid. Ammoniation of this mixture of phosphate species occurs within the reactor, as well, resulting in an aqueous solution containing ammonium ortho, pyro, tripoly, tetrapoly and some higher chain and cyclic phosphate species. These condensed phosphates generally exhibit increased water solubility as compared to orthophosphates and, consequently, more highly concentrated solutions can be prepared when they are present. The relative concentrations of the various species depends primarily on the temperature and pressure achieved within the reactor. Commercial solutions generally contain from about 34% to about 37% phosphorus pentoxide. Phosphorus pentoxide concentrations above about 37% approach water solubility limits resulting in solutions that are not stable, from which solids may precipitate during ambient temperature storage. Solutions of this type are generally referred to as either 10-34-0 or 11-37-0 liquid concentrates; the numerical designation refers to the percentage of their plant nutrient composition, i.e., ammoniacal nitrogen, phosphorus pentoxide and potassium oxide.

It should be noted that the condensed phosphates that are present in liquid concentrate solutions are subject to hydrolyses, which results in de-polymerization. The rate of hydrolytic degradation increases with time,

temperature, and the relative acidity of the solution. Therefore, ammonium polyphosphate concentrates and their solutions may vary in species composition as received, and as time progresses during their subsequent storage.

These liquid concentrates may additionally contain small amounts of diammonium sulfate and a host of metal and alkali-metal impurities. The quantity and quality of these impurities vary with the composition of the phosphate ore, the utilized process and the extent of purification that is conducted during manufacture of the wet-process phosphoric acid. Since these solutions are manufactured primarily as nutrients, the quality control parameters of greatest interest are the percentages of their contained nutrients - nitrogen and phosphorus - and the clarity, stability and color of the solution rather than purity per se.

The corrosion inhibiting system of the invention is comprised of at least one corrosion inhibiting compound selected from a group of corrosion inhibiting compounds consisting of azoles, insoluble ferric pyrophosphate, soluble ferric pyrophosphate, ferrous oxalate, ferric citrate, ferrous sulfate, ferric ammonium citrate, insoluble ferric orthophosphate, soluble ferric orthophosphate, ferric ammonium oxalate, ferric ammonium sulfate, ferric bromide, ferric sodium oxalate, ferric stearate, ferric sulfate, ferrous acetate, ferrous ammonium sulfate, ferrous bromide, ferrous gluconate, ferrous iodide, ferric acetate, ferric fluoroborate, ferric hydroxide, ferric oleate, ferrous fumarate, ferrous oxalate, ferrous oxide, ferric lactate, ferric resinate, and any combination thereof. In one preferred embodiment, the corrosion inhibiting system is comprised of at least one soluble corrosion inhibiting compound and at least one insoluble corrosion inhibiting compound. The combination of such soluble and insoluble corrosion

inhibiting iron containing compounds appears to provide the optimum combination of corrosion inhibition.

A minor amount of the corrosion inhibiting system of the invention effective to substantially reduce the corrosiveness of the fire retardant composition is included in the corrosion-inhibited fire retardant compositions of the invention. A minor effective amount of the corrosion inhibiting system is that amount, which substantially reduces the corrosivity of the fire retardant. As is understood by one of ordinary skill in the art, what constitutes a substantial reduction in corrosivity is largely dependent on the specific fire retardant used in the fire retardant composition of the invention, as well as the specific composition of the corrosion inhibiting system, and can be readily determined by one of skill in the art without undue experimentation.

In one embodiment, the corrosion inhibiting system of the invention is present in a minor amount effective in the corrosion-inhibited fire retardant composition, in concentrate, to obtain a retardant having at least one of a maximum corrosivity to aluminum of 5.0 mpy, yellow brass of 5.0 mpy, and steel of 5.0 mpy, as determined by the "Uniform Corrosion Test" set forth in Section 4.5.6.1.2 of "Specification 5100-304b (January 2000) Superseding Specification 5100-304a (February 1986)," entitled "Specification For Long Term Retardant, Wildland Fire, Aircraft or Ground Application," issued by the USDA.

In a specific embodiment, the corrosion inhibiting system of the invention comprises in the range of about .01% to about 10.0% of the total corrosion-inhibited fire retardant. In another specific embodiment, the corrosion inhibiting system of the invention comprises in the range of about 0.3% to about 6.0% of the total corrosion-inhibited fire retardant. In yet another specific embodiment,

the corrosion inhibiting system of the invention comprises in the range of about 0.6% to about 5.0% of the total corrosion-inhibited fire retardant.

Prior to use, and in one embodiment of the invention, the corrosion-inhibited compositions of the invention are blended with water to form dilute solutions containing the amount of phosphorus pentoxide required to achieve the maximum amount of vegetation coverage at an application rate sufficient to reduce the flammability of the vegetative fuels to the desired level. The water used in the composition of the invention may be tap water, or water from other convenient water sources. Generally, the compositions are diluted one part concentrate to in the range of about three to seven parts water. In a specific embodiment, the compositions of the invention are diluted one part concentrate to in the range of about four to six parts water. However, it should be noted that the compositions of the invention may be diluted outside of the above ranges, for example where improved retardant penetration is desired. In a specific embodiment, the fire retardant compositions of the invention comprise less than about 1.18% biopolymer in dilute solution.

In a specific embodiment, the compositions of the invention are blended with water to form dilute solutions containing the amount of phosphorus pentoxide required to meet USDA, Forest Service Specification fire-retardant effectiveness requirements. This concentration, which is determined via combustion-retarding effectiveness testing described in USDA, Forest Service Specification 5100-304b, "4.5.2. Combustion Retarding Effectiveness Test," will generally depend on the percentage of phosphorus pentoxide present in the concentrated composition, and the extent of its availability for retarding reactions. The corrosion-inhibited fire retardant composition of the invention is

typically diluted to an amount effective to achieve maximum coverage of vegetation at an application rate sufficient to reduce the flammable fuels to a desired level. The minimum USDA, Forest Service Specifications, for combustion retarding effectiveness, as specified in Specification 5100-304b, is generally obtained when the corrosion-inhibited fire retardant concentrate of the invention is diluted with about 1 to about 8 volumes of water.

To suppress wildland fires, the corrosion-inhibited fire retardant compositions of the invention are diluted with water and applied on threatened vegetation, ahead of approaching wildland fire. Ammonia from both the ammonium phosphate and the ammonium sulfate are liberated at temperatures below the ignition temperature of the fuel. The phosphoric and sulfuric acids are both initially effective fire retarding acids. The phosphoric acid will remain present and effective with the vegetative fuel until temperatures exceed 600°C. However, the boiling point of sulfuric acid is much lower, and the amount present will decrease as the fuel temperature increases. Thus, at least a portion of the sulfuric acid is lost prior to the ignition temperature of the fuel. The resultant mineral acids subsequently react with the cellulosic components of vegetative fuels on which they are applied. Their thermal decomposition is thereby altered in such a manner that they will no longer serve as fuel. These reactions are described in U.S. Pat. No. 4,839,065 to Vandersall, which is hereby incorporated by reference in its entirety.

The fire retardant compositions of the invention may also contain suspending agents. Suspending agents effectively reduce the rate of separation and settling during long term storage. Thus, as one skilled in the art would appreciate, the amount of suspending agent depends upon its relative

effectiveness per unit applied, the desired length of storage and the additional additives incorporated into the compositions of the invention. As used herein, suspending agents useful in the compositions of the invention include colloidal clays, for example, attapulgus, fuller's earth, sepiolite, montmorillonite, and kaolin clays. As used herein, attapulgus clay includes, but is not limited to attapulgite and polygorskite. As used herein, kaolin clay includes, but is not limited to Kaolinite, $[Al_2Si_2O_7\text{-}2(H_2O)]$ and $[Al_2O_3\text{-}2SiO_2\text{-}2(H_2O)]$.

As will be apparent to those skilled in the art, the corrosion-inhibited fire retardant of the invention may contain or be mixed with other functional components or additives such as suspending agents, coloring agents, surfactants, stabilizers, opacifying agents, other corrosion inhibitors, any combination thereof, or with other functional components.

For example, and in one embodiment of the invention, the corrosion-inhibited fire retardant composition of the invention includes at least one highly colored pigment. The colored pigment is incorporated to assist in the visual identification of treated and untreated vegetation. Suitable highly colored pigments include iron oxide, which produces many colors like brown and red, titanium dioxide pigments, which produce a white color, or an ultra-violet sensitive dye dispersed in biodegradable plastic. However, for certain uses, like along roadsides or in parks, it may be desirable to exclude any colorant from the mixture. Accordingly, as one skilled in the art would appreciate, the amount of colorant or pigment incorporated into the compositions of the invention depends on the degree of the dilution and visibility contemplated by the user. Visibility is usually obtained with red iron oxide when it is present in the diluted solution in the range of about 0.15% to about 0.4%, depending on the colorant characteristics

and on the vegetative and topographical characteristics of that on which it will be applied. The amount incorporated in the concentrate will, of course, vary with the dilution rate required to provide adequate fire retarding effectiveness.

In another embodiment, the present invention includes at least one of red iron oxide or brown iron oxide, or a combination thereof. In yet another embodiment, the present invention includes a fugitive coloring agent, whose color fades upon exposure to the elements. In a further embodiment, the present invention includes opacifying pigments, which are generally not highly colored, but have the ability to cover and hide that on which it is deposited so that the highly colored pigment becomes more visible.

Surfactants may also be added to increase visibility, through the generation of a foam, and to improve penetration of the retardant solution into porous fuels. Accordingly, as one skilled in the art would appreciate, the amount and type of surfactant incorporated into the compositions of the invention depends on the degree of the dilution and visibility contemplated by the user.

Thickeners, for example, hydroxypropyl guar, may also optionally be added to the compositions of the invention. The existence of such gums in the compositions of the invention is not necessary for anti-corrosive or improved rheological characteristics to be realized. If employed, the quantity of other gums in the compositions of the invention will vary depending in part on the nature and concentration of the fire-retardant salts present, the presence of impurities, and the presence of other components. Accordingly, and in one embodiment of the invention, the compositions of the invention contain thickeners, for example, hydroxypropyl guar, or other non-ether derivative guar thickeners. In other

embodiments of the invention, the compositions do not contain thickeners, for example, hydroxypropyl guar.

It has been discovered that azoles are effective corrosion inhibitors for brass. In one embodiment of the invention, the compositions of the invention comprise at least one azole. As used herein, an azole is any of a group of chemical compounds with a five-membered ring containing one or more nitrogen atoms. Azoles suitable for use in the corrosion-inhibited fire retardants of the invention include, but are not limited to tolytriazole, benzotriazole, mercaptobenzothiazole, dimercaptothiadiazole, 1,2 benzisothiazoline-3-1, 2-benzimidazolone, 4,5,6,7-tetrahydrobenzotriazole, tolylimidazole, 2-(5-ethyl-2-pyridyl) benzimidazole, phthalimide, any alkali metal salts thereof and combinations thereof. The amount of azole or other corrosion inhibitor is dependent upon the corrodible metal for which corrosion resistance is desired, the level of resistance desired, and the specific concentration of the fire retardant composition employed, including corrosion inhibiting compounds contained therein.

However, in one embodiment of the invention, the corrosion-inhibited fire retardant concentrates include at least one azole, present in a minor amount effective to obtain a corrosivity of yellow brass to a maximum of 5.0 mpy, as determined by the "Uniform Corrosion Test" set forth in Section 4.5.6.1 of "Specification 5100-304b (January 2000) Superseding Specification 5100-304a (February 1986)," entitled "Specification For Long Term Retardant, Wildland Fire, Aircraft or Ground Application," issued by the USDA. In a specific embodiment of the invention, the fire retardant concentrates of the invention comprise in the range of about .01% to about 1.0% tolytriazole. In yet another

specific embodiment, the compositions of the invention include in the range of about 0.2% to about 0.6% tolytriazole. In yet another specific embodiment, the compositions of the invention include in the range of about 0.3% to about 0.5% tolytriazole.

A method of inhibiting corrosion using the above-described corrosion inhibiting system of the invention is also provided. According to the method of the invention, a corrodible material is provided and contacted with an effective amount of the corrosion inhibiting system of the invention to substantially reduce the corrosiveness of the fire retardant.

In one embodiment of the invention the corrodible material is also contacted with at least one above-described suspending agents. In another embodiment, the method of inhibiting corrosion further includes the step of contacting the corrodible material with at least one above-described biopolymer having a particle size less than about 100 microns. Accordingly, the method includes providing a corrodible material and contacting the corrodible material and at least one above-described biopolymer having a particle size less than about 100 microns and an effective amount of the corrosion inhibited system of the invention.

Any corrodible material may be used according to the method of inhibiting corrosion of the invention. In one embodiment, the corrodible material is selected from a group of corrodible materials consisting of steel, brass, aluminum, and any alloy thereof.

Prior to use, and in one embodiment of the invention, the corrosion inhibiting system and biopolymer, if present, are blended with water prior to or

during contact with the corrodible material. The water used in the composition of the invention may be tap water or water from other convenient water sources.

In one embodiment, the corrosion inhibiting system of the invention includes at least one additive selected from a group of additives including suspending agents, coloring agents, surfactants, opacifying pigments, stabilizers, corrosion inhibitors and any combination thereof.

While the corrosion-inhibited fire retardant compositions of the invention reduce aluminum corrosivity in the absence of biopolymers, biopolymers are not significantly effective for reducing corrosion to aluminum in the absence of the corrosion inhibiting system of the invention. However, it has been discovered that the corrosion-inhibited fire retardant composition of the invention containing biopolymers shows improved rheological characteristics in the absence of the corrosion-inhibiting system of the invention. Specifically, increased viscosity is shown in dilute solutions comprising the above-described corrosion-inhibited fire retardant composition, in the absence of the corrosion inhibiting system of the invention. Accordingly, in one embodiment, fire retardant composition of the invention comprises at least one above-described fire retardant composition comprised of at least one ammonium polyphosphate and at least one above-described biopolymer having a particle diameter of less than about 100 microns. This embodiment, which does not include the above-described corrosion inhibiting system of the invention, will hereinafter be referred to as the viscosity-increased fire retardant compositions of the invention.

While suspending agents may be utilized in all of the fire retardant compositions of the invention, the use of suspending agents is not necessary for improved rheological characteristics to be realized in both the concentrated and

dilute fire retardant compositions, or for the corrosion inhibiting characteristics of the corrosion-inhibited fire retardant compositions of the invention to be realized.

The viscosity-increased fire retardant compositions of the invention generally comprise in the range of about .01% to about 5.0% biopolymer, in concentrate composition. However, as one skilled in the art will appreciate, compositions comprising biopolymer concentrations outside of this range are also effective in increasing the viscosity of fire retardant compositions. In one specific embodiment of the invention, the viscosity-increased fire retardant composition of the invention, in concentrate, comprises about 1.0% biopolymer. In another specific embodiment of the invention, the fire retardant composition, in concentrate, comprises about 3.0% biopolymer.

In one specific embodiment, the viscosity-increased fire retardant compositions of the invention include at least one above-described xanthan biopolymer. In a specific embodiment, the fire retardant compositions of the invention include at least one fire retardant composition comprised of at least one ammonium polyphosphate, in the range of about .01% to about 5.0% at least one xanthan biopolymer having a particle size less than about 100 microns, and at least one above-described additive or functional component.

The viscosity-increased fire retardant compositions of the invention are prepared in the same manner as the above-described corrosion-inhibited fire retardant composition of the invention. Accordingly, and in one embodiment of the invention, the viscosity-increased fire retardant compositions of the invention are prepared by forming an intermediate concentrate composition comprising the above-described fire retardant composition containing at least one ammonium

polyphosphate and at least one above-described biopolymer having a particle size less than about 100 microns, and diluting the intermediate concentrate with water to form the viscosity-increased fire retardant composition of the invention. In one embodiment the compositions comprise less than about 1.18% biopolymer.

In a specific embodiment, the fire retardant compositions of the invention are prepared by forming an intermediate concentrate composition comprised of at least one above-described fire retardant and at least one xanthan biopolymer having an average particle diameter less than about 100 microns, wherein the fire retardant compositions comprise in the range of about .01% to about 5.0% xanthan biopolymer, and diluting the intermediate concentrate with water to form the increased-viscosity fire retardant composition of the invention.

A method of suppressing wildland fires using the viscosity-increased fire retardant compositions of the invention is also provided. The method includes the steps of aerially applying to wildland vegetation a fire suppressing composition comprising water and the above-described viscosity-increased fire retardant composition. In a specific embodiment, the method includes aerially applying to wildland vegetation a fire suppressing composition comprising water, at least one ammonium polyphosphate composition, less than about 1.18% of at least one xanthan biopolymer having a particle size less than about 100 microns and at least one above-described additive.

All references and patents cited herein are hereby incorporated by reference in their entireties for their relevant teachings. Accordingly, any reference cited herein and not specifically incorporated by reference is,

nevertheless, incorporated by reference in its entirety as if part of the present specification.

The following examples illustrate specific embodiments of the invention without limiting the scope of the invention in any way. In each example, samples of ammonium polyphosphate fire retardant concentrates were mechanically admixed with iron containing compounds, biopolymer, additives, and in some cases, with an azole, as indicated in each table. Any mechanical mixing technique that is well known in the art may be used in the present invention. The concentrated fire retardant solutions are diluted with water, as indicated. The "Requirements" row illustrates the level of aluminum 2024-T3 corrosion allowed by the USDA, Forest Service Specifications 5100-304b, i.e., the maximum allowable corrosivity for product acceptance for use in wildland fire retardant compositions. The resulting samples were tested for corrosivity in accordance with USDA, Forest Service Specifications 5100-304b.

EXAMPLE 1-THE ALUMINUM CORROSIVITY OF NEAT AMMONIUM POLYPHOSPHATE SOLUTION

Table 1 illustrates the corrosion characteristics of neat, unadulterated fertilizer grade 10-34-0 and 11-37-0 ammonium polyphosphate liquid concentrates obtained from three different sources. All of the samples are either 10-34-0 or 11-37-0, as received, with no additions. The corrosivity of the samples were expressed in mils of metal loss on exposed metal surface extrapolated from 90 to 365 days (mpy) and ascertained using the aforementioned USDA, Forest Service Specifications for determining corrosivity. Both the concentrated retardant and its diluted solutions were tested at each temperature and condition indicated.

The diluted solutions were prepared by admixing four to five volumes of water with one volume of the concentrated solution. Thus, the diluted solutions were in the range of between about 15% to about 20% by volume of the concentrate.

In accordance with the Forest Service Specifications for corrosion testing of fire retardants, a one-inch wide, four-inches long, one-eighth inch thick coupon of the aluminum was obtained from a standard source. The coupon is cleaned, dried and weighed according to standard USDA, Forest Service Specifications and suspended in a one quart, straight sided jar filled either 50% (partially) or 100% (totally) full using a piece of nylon string. When suspended in a partially full jar, the coupon was 50% (two inches) immersed in the test solution with the other 50% extending up from the solution into the air space above it. When the jar was full with approximately 800 ml of the solution, the metal coupon was totally immersed in the solution. The jars were then closed with a screw cap and two or three identical corrosion jars (cells) of each partially and totally immersed coupons were stored at 70°F and 120°F for ninety days. At the end of the ninety day storage period, the jars were opened and the coupons were removed and cleaned according to the USDA, Forest Service Specifications. The coupon was then re-weighed after it dried and its weight loss was determined by comparing its initial and final weights. The calculated weight loss and density of the metal coupon were used to extrapolate to mils (0.001 inches) of aluminum that would be lost during a one-year period at the test condition, assuming that the weight loss was experienced uniformly across the coupon surface. The corrosion rate of both the partially and totally immersed coupons were calculated using the total

surface area of the coupon. The samples at each condition were then averaged and reported as the corrosion rate. The results are shown in Table 1.

Table 1

	Aluminum Corrosivity when tested in the indicated configuration (mpy)							
	Neat Concentrate				Diluted Solution			
Ammonium Polyphosphate Samples	70°F total	70°F partial	120°F total	120°F partial	70°F total	70°F partial	120°F total	120°F partial
Requirements	≤5.0	≤5.0	≤5.0	≤5.0	≤2.0	≤2.0	≤2.0	≤2.0
Sample 1	8.7	4.3	134.3	77.8	8.4	6.5	24.9	5.7
Sample 2	12.4	6.6	106.6	78.5	15.2	8.4	10.1	5.6
Sample 3			146.0				5.8	
Sample 4	8.1	4.1	140.7	67.4	5.8	6.3	11.4	7.8
Sample 5			129.4				11.0	
Sample 6			170.0				10.8	
Sample 7			168.5				7.4	
Sample 8	10.2	5.3	165.0	88.6	12.3	6.4	21.8	13.3
Sample 9	10.9	5.5	161.4	85.3	12.0	7.0	39.0	14.8
Sample 10			130.0				21.1	
Sample 11			126.2				22.8	
Sample 12	4.3		109.4		11.0		6.4	
Sample 13			149.4				33.7	
Sample 14	9.5		155.6		12.7		35.8	
Sample 15	12.7	6.0	201.0	96.5	12.8	7.5	35.8	19.3
Sample 16	13.1	7.1	159.0	86.7	11.2	6.5	42.7	21.8
Sample 17			151.5				13.3	
Sample 18			136.3				29.2	
Sample 19	12.0	6.3	144.8	94.5	17.7	10.4	10.5	7.0
Sample 20	9.9		115.8		13.8		12.4	
Sample 21	15.2		176.9		12.7		35.1	
Sample 22	10.9	5.5	172.6	74.8	13.1	7.2	42.9	18.3
Average	10.6	5.6	147.7	83.3	12.2	7.4	22.0	12.6
Range (Lo-Hi)	4.3-15.2	4.1-7.1	106.6-201.0	67.4-94.5	5.8-17.7	6.3-10.4	5.8-42.9	5.6-21.8

The corrosivity of the ammonium polyphosphate solutions to aluminum 2024T-3 was relatively low when the temperature was maintained at about 70°F. However, none of the samples of the neat ammonium polyphosphate solutions met the Forest Service Specifications for corrosivity of fire retardants. In addition, the results showed that increasing the solution temperature to 120°F dramatically increased the corrosion of the aluminum coupon by the neat ammonium polyphosphate samples, i.e., in excess of an order of magnitude.

EXAMPLE 2-THE ALUMINUM CORROSIVITY OF AMMONIUM POLYPHOSPHATE SOLUTION CONTAINING 1.2% IRON OXIDE (Fe_2O_3) & 1.4% ATTAPULGUS CLAY

The corrosion characteristics of neat fertilizer grade ammonium polyphosphate solutions containing additional amounts (<3%) of a mixture of an iron oxide colorant and attapulgus clay is illustrated in Table 2. Each sample was prepared by admixing neat concentrated ammonium polyphosphate obtained from several sources with 1.4% attapulgus clay, and either 1.2% red iron oxide or 1.2% brown iron oxide, as indicated. In addition, 0.3% tolytriazole was also admixed into Samples 11, 15, 16, 18 and 19 and 0.5% tolytriazole was admixed into sample 20. Aliquots from these concentrate samples were then diluted by admixing 1.0 volume of concentrate with 4.25 volumes of tap water. The concentrates and their solutions were then tested for corrosivity and diluted in accordance with Forest Service Specifications. The results are shown in Table 2.

Table 2

Ammonium Polyphosphate Samples	Type of Iron Oxide	Corrosion Rate (milli-inches per year)							
		Neat Concentrate				Diluted Solution			
		70°F total	70°F partial	120°F total	120°F partial	70°F total	70°F partial	120°F total	120°F partial
Corrosion of neat 10-34-0 Average from Table1	none	10.6	5.6	147.7	83.3	12.2	7.4	22.0	12.6
Requirements		≤5.0	≤5.0	≤5.0	≤5.0	≤2.0	≤2.0	≤2.0	≤2.0
Sample 1	Bn Iron oxide(1)			1.4				4.4	
Sample 2	Bn Iron oxide(1)			0.7				3.7	
Sample 3	Bn Iron oxide(1)			1.4				2.3	
Sample 4	Bn Iron oxide(1)			6.4				10.1	
Sample 5	Rd Iron oxide(2)	4.6	3.6	7.3	5.0	6.7	4.4	4.0	3.6
Sample 6	Rd Iron oxide(2)	3.5	1.9	6.7	9.0	4.3	3.9	2.5	3.3
Sample 7	Rd Iron oxide(2)			2.3				4.5	
Sample 8	Rd Iron oxide(2)	3.5	3.8	1.7	1.6	2.8	4.3	3.5	3.6
Sample 9	Rd Iron oxide(2)			3.0				3.1	
Sample 10	Rd Iron oxide(2)			15.3				11.7	
Sample 11	Rd Iron oxide(2)			32.1				7.1	
Sample 12	Rd Iron oxide(2)			8.3				3.8	
Sample 13	Rd Iron oxide(2)			26.3				3.9	
Sample 14	Rd Iron oxide(2)			19.7				3.8	
Sample 15	Rd Iron oxide(2)			4.3				0.8	
Sample 16	Rd Iron oxide(2)			6.7				5.3	
Sample 17	Rd Iron oxide(2)			2.3				4.2	
Sample 18	Rd Iron oxide(2)	1.4		8.0		2.7		2.0	
Sample 19	Rd Iron oxide(2)	5.0	3.5	8.5	13.7	5.7	4.2	5.4	4.1
Sample 20	Rd Iron oxide(2)	4.4	2.4	11.2	2.8	4.1	4.0	2.3	2.8
Sample 21	Rd Iron oxide(2)			2.0				1.9	
Sample 22	Rd Iron oxide(2)			7.8				11.1	
Average		3.7	3.0	8.3	6.4	4.4	4.2	4.6	3.5
Range		1.4-5.0	1.9-3.8	0.7-32.1	1.6-13.7	2.7-5.7	3.9-4.3	2.5-11.7	2.8-4.1

(1) Brown iron oxide, Lot number 5594050A, Elementis Pigments No. 8690.
(2) Red iron oxide, Lot number 5891719A, Elementis Pigments R03097 precipitated Kroma red pigment

The results indicated that the addition of small amounts of iron oxide and clay reduced the corrosion of totally immersed aluminum in a 70°F solution by 50% to 65%. In addition, the impact of the mixture on high temperature corrosion was even more dramatic than at low temperature. When the corrosion cell was stored at 120°F, the rate of aluminum corrosion decreased by about 75% to 90%. At both temperatures the corrosion rate on partially immersed coupons was greater than 50% of the totally immersed values, which indicated that significant interface or vapor/air phase corrosion occurs when the mixture is present in the solution. This differs from the corrosivity of the neat ammonium polyphosphate solutions of Table 1. However, the addition of 1.2% insoluble iron oxide and a suspending clay to the ammonium polyphosphate samples did not reduce the aluminum 2024-T3 corrosion rate of the concentrates or its solutions to within the limits required by the USDA, Forest Service Specifications.

EXAMPLE 3-THE ALUMINUM CORROSIVITY OF AMMONIUM POLYPHOSPHATE SOLUTIONS CONTAINING A MIXTURE OF SOLUBLE AND INSOLUBLE IRON COMPOUNDS

The data in Tables 3a and 3b illustrate the relative effectiveness of a number of corrosion inhibitor systems containing water soluble and water insoluble sources of iron, and mixtures thereof, in several sources and types of ammonium polyphosphate concentrates and their diluted solutions. The samples were prepared by admixing either 10-34-0 or 11-37-0 type ammonium polyphosphate solutions from various sources with varying concentrations of insoluble red iron oxide or brown iron oxide additives and attapulgus clay additives and varying the concentrations of other iron containing additives, as indicated. The solutions were subjected to high shear mixing in order to activate or hydrate the clay.

Each concentrate and its diluted solution was tested for aluminum corrosivity in accordance with the Forest Service Specification protocols. The results are shown in Tables 3a and 3b.

Table 3a

CORROSION (mpy)

	Ammonium Polyphosphate Samples	Insoluble Iron Oxide Added		Other Iron Containing Additive				Neat Concentrate				Diluted Solution			
						Fe. Content		70°F	70°F	120°F	120°F	70°F	70°F	120°F	120°F
		%	Type	(%)	Additive	% insol.	% sol.	Total	partial	total	Partial	total	partial	total	partial
1	SAMPLE 1 (from Table 1)	0.0	None	0.0	None	0.00	0 00	9.1	5.2	140.6	79.5	10.8	6.9	16	9.4
2		1.2	Iron oxide	0.0	None	0.00	0.00	3.7	3	8.3	6.4	4.4	4.2	4.6	3.5
3		0.6	Br. Iron oxide	3.0	Sol. Ferric pyrophosphate	0.42	0.35			7.4				0.5	
4		0.6	Br. Iron oxide	5.0	Sol. Ferric pyrophosphate	0.42	0.58			9.0				0.6	
5		1.2	Br. Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			2.2				1.0	
6		1.2	Br. Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0 35			2.2				1.0	
7		1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			5.7				1.3	
8		1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			10.9				2.5	
9		1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			10.8				1.6	
10		1.2	Red Iron oxide	3.0	Sol Ferric pyrophosphate	0.84	0.35			10.3				1.5	
11		1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate*	0.84	0.35			18.1				1.6	
12		1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate*	0.84	0.35	3.1	3.1	6.1	2.9	4.4	3.6	1.6	3.4
13		0.6	Br. Iron oxide	0.6	Sol. Ferric citrate*	0.42	0.13			118.7				1.4	
14		0.6	Br. Iron oxide	3.0	Sol. Ferric citrate	0.42	0.66			5.5				0.6	
15		0.6	Br. Iron oxide	3.0	Sol. Ferric citrate*	0.42	0.66			6.7				0.6	
16		1.2	Br. Iron oxide	1.8	Sol. Ferric citrate*	0.84	0.40			0.9				0.5	
17		1.2	Br. Iron oxide	1.8	Sol. Ferric citrate*	0.84	0.40			15.3				3.3	
18		1.2	Red Iron oxide	1.8	Sol. Ferric citrate*	0.84	0.40			46.5				2.2	
19		1.2	Br. Iron oxide	3.0	Sol. Ferric citrate*	0.84	0 66			1.0				0.7	
20		1.2	Br. Iron oxide	3.0	Sol. Ferric citrate	0.84	0.66			4.5				0.7	
21		1.2	Br. Iron oxide	3.0	Sol. Ferric citrate	0.84	0.66			3.9				0.6	
22		1.2	Br. Iron oxide	3.0	Sol. Ferric citrate	0.84	0.66			1.0				0.7	
23		0.6	Br. Iron oxide	5.0	Sol. Ferric NH4 citrate	0.42	0.88			7.9				0.8	
24		1.2	Red Iron oxide	1.8	Sol. Ferric NH4 citrate	0.84	0.32			53.9				3.4	
25		1.2	Red Iron oxide	3.0	Sol. Ferrous sulfate•7H20	0.84	0.60			1.0				3.4	
26		1.2	Red Iron oxide	1.2/3.0	Insol./sol. Ferric pyrophosphate	1.13	0.35			7.5				1.3	
27				1.2/3.0	Insol./sol. Ferric pyrophosphate	0.29	0.35			2.0				1.2	
28				1.2/3.0	Insol./sol. Ferric pyrophosphate	0.29	0.35			2.3				0.7	
29				3.0/3.0	Insol./sol. Ferric pyrophosphate	0.72	0.35			5.8				1.0	
30				1.2/3.0	Insol ferric pyro/sol. Fe citrate	0.29	0.66			2 1				1.2	
31				1.2/3.0	Insol ferric ortho/sol Ferric pyro	0.37	0.35			3.1				1.5	

*These compositions contain 0.3-0.5% tolytriazole for brass corrosion inhibition.

Table 3b

CORROSION (MILS PER YEAR)

	Ammonium Polyphosphate	Insoluble Iron Oxide Added		Other Iron Containing Additive				Neat Concentrate				Diluted Solution			
						Fe. Content		70°F	70°F	120°F	120°F	70°F	70°F	120°F	120°F
	Samples	%	Type	(%)	Additive	% insol.	% sol.	total	partial	total	partial	total	partial	total	partial
32	SAMPLE I			I.2/3.0	Insol ferric ortho/sol Ferric pyro	0.37	0.35			2.2				I.0	
33				1.2/3.0	Insol/sol. Ferric ortho	0.37	0.41			1.9				2.2	
34				1.2/3.0	Insol/sol. Ferric ortho	0.37	0.41			I.9				1.5	
35				I.2/4.0	Insol. Fe(III) orthophosphate/sol Fe(III) NH4 citrate	0.37	0.70			2.3				1.4	
36				1.2/4.0	Insol. Fe(III) orthophosphate/sol Fe(III) NH4 citrate	0.37	0.70			I.8				1.2	
37				1.2/3.0	Insol. Fe oxalate 2H20/sol. Ferric pyrophosphate	0.37	0.35			17.0				1.9	
38				1.2/3.0	Insol. Fe oxalate/sol. Fe sulfate	0.37	0.60			37.4				5.8	
39	SAMPLE 2	1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35	1.2	0.9	10.1	5.2	3.7	3.7	1.4	1.7
40		1.2	Br. Iron oxide	3.0	Sol. Ferric citrate	0.84	0.66			0.2				0.4	
41	SAMPLE 3	0.6	Br. Iron oxide	5.0	Sol. Ferric citrate	0.42	1.10			6.2				0.5	
42		1.2	Br. Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.45	2.8	2.7	110.1	70.2	11.0	6.7	7.6	3.5
43		1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			33.2				7.6	
44	SAMPLE 4	1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35	3.7		76.5		6.4		0.8	
45	SAMPLE 5[2]	1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35	2.3		2.8		2.8		1.1	
46		1.2	Red Iron oxide	4.0	Sol. Ferric pyrophosphate	0.84	0.46	1.8		2.8		2.6		1.8	
48		2.4	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	1.68	0.35	I.4		2.1		2.7		1.2	
49		1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			4.0				2.1	
50		1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35	I.6	1.0	2.4	I.7	2.0	3.2	1.1	2.0
5I		1.2	Red Iron oxide	3.0/3.0	insol./sol. Ferric pyrophosphate	1.56	0.56	0.6		5.4		1.6		0.9	
52	SAMPLE 6[2]	1.2	Br. Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35	2.I	1.7	113.0	52.7	11.8	6.2	8.1	4.5
53		1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			21.0				5.6	
54	SAMPLE 7[2]	1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35	4.2		83.0		3.8		I.1	

(1) These compositions contain 0.3-0.5% tolytriazole for brass corrosion inhibition.
(2) 11-37-0 type Ammonium Polyphosphate Sample

For comparative purposes, line 1 illustrates the average corrosion characteristics of neat concentrate and dilute solutions from Sample 1, taken from Table 1, and line 2 illustrates the corrosion of the concentrate and diluted solutions when 1.2% iron oxide and 1.4% attapulgus clay, with the exception of the formulations on line 9 which contained 0.7% attapulgus clay and the formulation on line 11, which contained 2.8% attapulgus clay, was mixed with the neat concentrate solution, see Table 2. Samples 1-4 were 10-34-0 type ammonium polyphosphate samples obtained from various sources. Samples 5-7 were 11-37-0 type ammonium polyphosphate samples obtained from various sources.

The data in Tables 1 and 2 illustrate that corrosive attack of aluminum was most severe when exposed to the fire retardant concentrate and its solutions at elevated (120°F/49°C) temperature in the totally immersed configuration. Consequently, the evaluation of corrosion inhibiting systems stressed testing under these conditions. Periodic testing at other conditions was conducted. Lines 3 through 6 illustrate the corrosion inhibiting effectiveness of combinations of insoluble brown iron oxide and soluble ferric pyrophosphate. The results indicated that the USDA, Forest Service Specifications for corrosivity of fire retardants were met when 1.2% of the brown iron oxide was used in conjunction with 3.0% of the soluble ferric pyrophosphate. In addition, the results indicated that lower amounts of the insoluble iron oxide resulted in unacceptable corrosion in the concentrated retardant solution.

Lines 7 through 12 illustrate the effectiveness of corrosion inhibiting systems similar to those described in the preceding paragraph, except red iron oxide is substituted for brown iron oxide. The results indicate that the red iron

oxide is effective in reducing the aluminum corrosion of the concentrated and diluted ammonium polyphosphate although perhaps not quite as effective as the brown iron oxide.

Lines 13-22 illustrate the corrosion inhibiting effectiveness of mixtures of insoluble iron oxide and soluble ferric citrate. The results indicated that ferric citrate was an equally effective substitute for soluble ferric pyrophosphate. In addition, the results indicate that a mixture of brown iron oxide and 3.0% soluble ferric citrate was capable of reducing the corrosivity of the ammonium polyphosphate samples to within acceptable levels for compliance with Forest Service Specifications for corrosivity of fire retardants.

Lines 23 and 24 illustrate the use of ferric ammonium citrate as a substitute for ferric citrate. The results indicated that the soluble ferric compounds were as effective as ammonium citrate in reducing corrosion of aluminum by ammonium polyphosphate solutions.

Lines 27 through 38 illustrate the effectiveness of systems in which only uncolored, soluble and insoluble iron containing compounds are used rather than the relatively highly colored persistent iron oxides. This is important where true fugitive retardants are desired, whereby the color gradually fades when exposed to natural sunlight and disappears so as not to permanently stain that on which it is applied.

Lines 26 through 38 illustrate the effectiveness of mixtures of soluble and insoluble ferric pyrophosphate. Acceptable aluminum corrosion properties were obtained when 3.0% of the former and 1.2% of the latter were used as the corrosion inhibiting system in an ammonium polyphosphate solution. The

results also indicate that an increased level of insoluble ferric pyrophosphate did not further reduce the corrosivity of the concentrate.

Lines 27 though 38 illustrate the aluminum corrosion inhibiting effectiveness of mixtures of the various soluble and insoluble iron compounds. Lines 37 and 38 revealed that, although effective, the tested ferrous salts were less effective at equivalent iron addition rates as compared to the ferric compounds.

Lines 39 through 44 illustrate the aluminum corrosion inhibiting effectiveness of various soluble and insoluble iron compounds when used in conjunction with 10-34-0 ammonium polyphosphate concentrates obtained from alternative sources. These data indicate that the amount and ratio of corrosion inhibitor necessary to reduce corrosivity to an acceptable level will need to be optimized dependent on the source and characteristics thereof.

Lines 45 through 54 illustrate the aluminum corrosion inhibiting effectiveness of the subject compounds when used in various sources of 11-37-0 type ammonium polyphosphate concentrate and their diluted solutions.

EXAMPLE 4-CORROSION CHARACTERISTICS OF AMMONIUM POLYPHOSPHATE SOLUTIONS CONTAINING WATER SOLUBLE IRON COMPOUNDS

Example 4 illustrates the effectiveness of water-soluble ferric pyrophosphate, ferric citrate and ferrous sulfate as aluminum corrosion inhibitors in ammonium polyphosphate solutions. In each sample, the indicated soluble iron compounds and 1.4% attapulgus clay were admixed with neat ammonium polyphosphate. Aliquots were subsequently drawn from the concentrate and diluted with the prescribed amount of water. The aluminum corrosivity of both the concentrated fire retardants and their diluted solutions was determined in

accordance with the aforementioned Forest Service Specifications. The results of this testing is shown in Table 4.

Table 4

Ammonium Polyphosphate Samples	Soluble Iron Added			Aluminum Corrosion(1)	
	(%)	Additive	Total Fe (%)	Concentrate	Dilute Solution
Average Sample from Table 1	0	None	0	106.6-170.0	5.8-39.0
1	0.6	Soluble ferric pyrophosphate	0.07	150.6	1.5
2	3.0	Soluble ferric pyrophosphate	0.35	42.5	1.6
3	3.0	Soluble ferric pyrophosphate	0.35	75.4	1.2
4	3.0	Soluble ferric pyrophosphate	0.35	69.3	1.3
5	2.4	Soluble ferric citrate	0.53	113.1	2.5
6	3.0	Soluble ferric citrate	0.66	124.1	2.4
7	3.0	Soluble ferric citrate	0.66	17.0	1.1
8	3.0	Ferrous sulfate•$7H_2O$	0.60	27.9	3.1

(1) Aluminum 2024T3 coupons tested in the manner described in USDA, Forest Service specification 5100-304b. Values obtained when the corrosion cell was maintained at 120°F (50°C) for 90 days with the coupon totally immersed therein. The data is expressed in milli-inches per year.

The results indicate that both soluble ferric and ferrous iron containing salts show utility as aluminum corrosion inhibitors in ammonium polyphosphate solutions. Relatively small concentrations (0.35%) of soluble iron derived from a soluble ferric pyrophosphate decreased the corrosion rate of totally immersed aluminum exposed to 120°F solutions of the diluted fire retardant to within the USDA Forest Service Specification requirements. The data illustrate that soluble iron containing compounds are most effective in controlling the corrosivity of diluted solutions. Since the corrosivity of both the concentrate and its diluted solutions is of importance, mixtures of water soluble and water insoluble iron compounds generally provide superior performance.

EXAMPLE 5-CORROSION CHARACTERISTICS OF AMMONIUM POLYPHOSPHATE SOLUTIONS CONTAINING OTHER WATER INSOLUBLE IRON COMPOUNDS

Table 5 illustrates the effectiveness of water insoluble ferric orthophosphate, insoluble ferric pyrophosphate and ferrous oxalate as aluminum corrosion inhibitors in ammonium polyphosphate concentrates and their diluted solutions. 1.4% attapulgus clay was mixed with the concentrated ammonium polyphosphate, with the exception of Samples 6 and 7 which contained 0.7% and 2.8% attapulgus clay, respectively. Samples 13, 18 and 24 contained, also, an insoluble iron oxide as a solution colorant. The resultant fire retardant concentrates and their diluted solutions were evaluated in terms of aluminum corrosivity in accordance with the USDA Forest Service Specification requirements. The results of the testing are shown in Table 5.

Table 5

	Ammonium Polyphosphate Samples	Iron Oxide Addition		Other Insol. Fe Additive		Total Fe. Content	Neat Concentrate				Diluted Solution			
							70°F	70°F	120°F	120°F	70°F	70°F	120°F	120°F
		%	Type	(%)	Additive	(%)	Total	partial	total	Partial	total	partial	total	partial
							Corrosion Rate (milli-inches per year)							
1	Neat 10-34-0(1)	0.0	None	0.0	None	0.00	9.1	5.2	140.6	79.5	10.8	6.9	16 0	9.4
2	Sample 1	0.0	None	1.2	Ferric pyrophosphate	0 29			2.9				1.7	
3	Sample 2	0.0	None	2.4	Ferric pyrophosphate	0.58			9.4				3.7	
4	Sample 3	0.0	None	3.0	Ferric pyrophosphate	0.72			3.5				1.1	
5	Sample 4	0.0	None	3.0	Ferric pyrophosphate	0.72			6.5				2.2	
6	Sample 5	0.0	None	3.0	Ferric pyrophosphate	0.72			2.1				1.4	
7	Sample 6	0.0	None	3.0	Ferric pyrophosphate	0.72			3.6				2.1	
8	Sample 7	0.0	None	3.0	Ferric pyrophosphate	0.72			1.0				1.7	
9	Sample 8	0.0	None	2.4	Ferric pyrophosphate	0.58			10.7				1.0	
10	Sample 9	0.0	None	3.0	Ferric pyrophosphate	0.72			5.5				6.3	
11	Sample 10	0.0	None	3.0	Ferric pyrophosphate	0.72	2.4		6.2		3.1		1.1	
12	Sample 11	0.0	None	3.0	Ferric pyrophosphate	0.72			3.4				1.3	
13	Sample 12	0.0	None	3.0	Ferric pyrophosphate	0.72			3.2				2.2	
14	Sample 13(2)	1.2	Red Iron oxide	0.0	None	0.84	3.7	3.0	8.3	6.4	4.4	4.2	4.6	3.5
15	Sample 14	1.2	Red Iron oxide	3.0	Ferric pyrophosphate	1.56	2.0	1.3	4.8	3.0	1.5	3.1	0.8	2.0
16	Sample 15	1.2	Red Iron oxide	3.0	Ferric pyrophosphate	1.56	1.6		6.2		1.6		1.0	
17	Sample 16	1.2	Red Iron oxide	3.0	Ferric pyrophosphate	1.56	2.5		0.7		2.5		0.6	
18	Sample 17	1.2	Red Iron oxide	3.0	Ferric pyrophosphate	1.56	1.9	1.2	0.5	0.2	1.1	2.4	0.8	1.9
19	Sample 18	1.2	Red Iron oxide	3.0	Ferric pyrophosphate	1.56	2.1		2.7		1.1		0.8	
20	Sample 19	0.0	None	1.2	Ferric orthophosphate	0.16			105.3				1.7	
21	Sample 20	0.0	None	1.8	Ferric orthophosphate	0.55			108.6				3.8	
22	Sample 21	0.0	None	2.4	Ferric orthophosphate	0.73			9.3				4.1	
23	Sample 22	0.0	None	3.0	Ferric orthophosphate	0.92			2.3				4.2	
24	Sample 23	1.2	Brown Iron oxide	3.0	Ferric orthophosphate	1.25			1.5				1.0	
25	Sample 24	0.0	None	1.2	Ferrous oxalate	0.37			90.0				2.7	

(1) Average values from Table 1.
(2) See Table 2

The corrosion inhibiting effectiveness of insoluble ferric pyrophosphate was shown by a comparison of the compositions containing only this component, lines 2-13, with line 1. The effectiveness was also shown by comparison with 1.2% red iron oxide, line 14. These comparisons illustrate the effectiveness of insoluble ferric pyrophosphate as an aluminum corrosion inhibitor for concentrated ammonium polyphosphate and its solutions. It was shown to be superior to red iron oxide when compared on an equal ferric iron level. Accordingly, the insoluble ferric pyrophosphate would be preferred in many applications since it is not highly colored like the conventional iron oxides, which result in highly visible and persistent discoloration of that on which it is applied. Consequently, inhibitor systems containing these components would be suitable for use in fugitive colored fire retardant formulations.

Lines 15-19 illustrate the further reduction in aluminum corrosion, which was obtained by combining iron oxide and ferric pyrophosphate in the same corrosion inhibiting system. The results indicated that several of these formulations met the USDA, Forest Service Specifications for corrosivity of aluminum in both the concentrate and dilute forms.

The data contained in lines 20 and 23 illustrate the effectiveness of insoluble ferric orthophosphate in inhibiting the corrosion of aluminum exposed to ammonium polyphosphate solutions. The results indicated that the pyrophosphate moiety may be somewhat superior to orthophosphate for inhibiting the corrosion of aluminum.

The data contained in line 24 indicates that increasing the ferric iron content of the corrosion inhibiting system by using mixtures of ferric

orthophosphate and iron oxide was also an effective way of meeting the USDA, Forest Service Specifications for corrosivity of aluminum.

The data contained in line 25 illustrates the aluminum corrosion inhibiting effectiveness of small amounts of ferrous (FeII) iron when incorporated in ammonium polyphosphate concentrates and their diluted solutions.

EXAMPLE 6-EFFECTIVENESS OF AZOLES AS CORROSION INHIBITORS IN AMMONIUM POLYPHOSPHATE FIRE RETARDANT COMPOSITIONS

Example 6 illustrates the effectiveness of azoles as yellow brass corrosion inhibitors in concentrated ammonium polyphosphate based fire retardant formulations and in their diluted solutions. Each sample was prepared by mixing 1.4% attapulgus clay, 1.2% red iron oxide and the indicated azole corrosion inhibitor with the neat, concentrated ammonium polyphosphate. Subsequently, the concentrates were diluted with water in the manner described herein. The samples were then tested in accordance with USDA Forest Service Specification requirements.

Table 6

THE IMPACT OF AZOLES ON THE CORROSION OF YELLOW BRASS EXPOSED TO CONCENTRATED AMMONIUM POLYPHOSPHATE AND ITS DILUTED SOLUTIONS.*

Corrosion Inhibiting System	Corrosion of exposed yellow brass (mpy)							
	Concentrated Retardant						Diluted Solution	
	70T**	70P	120T	120P	70T	70P	120T	120P
None	0.5	0.6	0.6	2.0	1.5	5.7	20.3	14.9
0.3% tolytriazole			0.2				0.3	
0.5% tolytriazole	0.0	0.1	0.1	0.1	0.0	0.0	0.0	0.0
0.25% sodium tolyl triazole***			0.2				0.1	
0.255% sodium tolyl-triazole +			0.2				0.1	
0.425% sodium tolyl- triazole+			0.2				0.1	
0.5% sodium tolyl- triazole***			0.1				0.2	
0.5% sodium triazole++	0.1	0.1	0.1	0.1	0.1	0.1	0.3	0.1
1.0% sodium triazole++	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1

* 10-34-0 containing 1.4% attapulgus clay and 1.2% red iron oxide in addition to the described inhibitor additive.

** 70 and 120 refer to the solution storage temperature in °F, T and P refer to total of partial immersion of the metal coupon in the retardant solution during storage.

*** from a 50% aqueous solution of sodium tolytriazole.

\+ from an 85% aqueous solution of sodium tolytriazole.

++ from 100% sodium triazole.

The results indicated that azoles, including both tolytriazoles and salts thereof, are effective corrosion inhibitors for yellow brass in ammonium polyphosphate concentrates and solutions. These data and others included in previous Examples illustrate the advantages of using azoles in conjunction with the iron containing inhibitors of this invention to reduce both aluminum and brass corrosivity of the fire retardant compositions to within desirable limits.

EXAMPLE 7-THE IMPACT OF XANTHAN BIOPOLYMER ON 11-37-0 BASED LIQUID CONCENTRATE RETARDANT FORMULATIONS

Table 7 illustrates the impact of xanthan (Keltrol BT®) on the viscosity and aluminum corrosion of ammonium polyphosphate fire retardant concentrates and their dilute solutions containing water soluble and water insoluble sources of iron, xanthan biopolymer having a particle size less than about 100 microns, additives and mixtures thereof, as indicated. The samples were prepared by admixing 11-37-0 type ammonium polyphosphate solutions with various concentrations of attapulgus clay, tolytriazole, iron oxide, xanthan gum, insoluble ferric pyrophosphate and soluble ferric pyrophosphate or sodium citrate, as indicated. The solutions were subjected to high shear mixing in order to activate or hydrate the clay, where necessary. Dilution was accomplished by admixing five volumes of water with one volume of the concentrated 11-37-0 or compositions based thereon. All references to xanthan in Tables 7a and 7b refer to a commercial grade of xanthan, Keltrol BT®, which has an average particle diameter less than about 100 microns.

Each concentrate and diluted solution was tested for aluminum corrosivity in accordance with the Forest Service Specification protocols and the viscosity of

each concentrate and diluted solution was tested by methods of testing viscosity that are well-known in the art. The results are shown in Tables 7a and 7b.

Table 7a

Formulation No. Components (wt.%)	USFS Corrosion Reqm'ts	A	B	C	D	E	F	G	H	I	J	K	L
Ammonium Polyphosphate (conc.)		100.0	99.0	97.1	96.1	94.1	93.1	91.1	90.1	91.1	90.1	97.5	94.5
attapulgus clay				1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4		
tolytriazole				0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Iron oxide				1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Keltrol BT-xanthan gum			1.0		1.0		1.0		1.0		1.0	1.0	1.0
Ferric pyrophosphate (insol)						3.0	3.0	3.0	3.0	4.3	4.3		3.0
Ferric pyrophosphate (sol)								3.0	3.0				
Sodium citrate										1.7	1.7		
Total		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Concentrate													
Viscosity (cps)*													
Initial		63	70	123	191	221	202	321	245	238	226	81	95
14 days		63	70	333	318	233	196	280	290	338	378	78	98
30 days		58	63	436	477	497	313	690	396	700	408	75	100
90 days		66	63	1000	1290	1310	1360	1200	740	1020	1510	66	88
Aluminum Corrosion (mpy)													
70T	≤5.0	6.7	6.3	1.1	2.6	0.6	0.3	0.6	0.7	0.8	0.8	7.2	2.0
70P	≤5.0	3.6	3.5	0.6	1.6	0.6	0.4	0.5	0.6	0.6	0.6	3.9	1.2
120T	≤5.0	110.4	105.4	5.9	4.7	0.9	0.9	1.6	1.7	1.1	1.1	48.4	1.5
120P	≤5.0	70.5	68.9	2.4	3.0	0.8	0.5	0.5	0.6	0.7	0.8	24.7	1.2
Dilute Solution (5:1 mix ratio)													
Viscosity (cps)*													
Initial		5	163	8	163	8	177	8	187	8	192	165	173
14 days		11	48	11	155	-	156	8	185	-	-	229	169
30 days		6	20	8	147	8	155	10	175	8	160	148	160
90 days		6	12	10	118	8	53	8	113	10	107	73	103
Aluminum Corrosion (mpy)													
70T	≤2.0	13.6	10.6	2.5	0.8	1.2	0.7	2.1	0.7	2.7	0.7	1.2	0.6
70P	≤2.0	7.8	6.2	3.4	2.5	2.1	1.6	2.0	1.6	2.0	1.5	2.7	4.4
120T	≤2.0	3.2	3.6	1.8	0.7	1.6	0.7	1.4	0.6	0.9	0.7	0.8	0.8
120P	≤2.0	5.4	4.4	3.4	2.1	2.3	1.5	2.4	1.5	2.0	1.3	1.9	2.5

* Samples stored at 90°F with steel coupon suspended therein. Sample homogenized prior to measuring viscosity

Table 7b

Formulation No. Components (wt.%)	USFS Corrosion Reqm'ts	M	N	O	P	Q	R	S
Ammonium Polyphosphate (conc)		97.0	94.1	91.1	88.1	88.1	95.5	92.5
attapulgus clay			1.4	1.4	1.4	1.4		
tolytriazole			0.3	0.3	0.3	0.3	0.3	0.3
Iron oxide			1.2	1.2	1.2	1.2	1.2	1.2
Keltrol BT-xanthan gum		3.0	3.0	3.0	3.0	3.0	3.0	3.0
Ferric pyrophosphate (insol)				3.0	3.0	4.3		3.0
Ferric pyrophosphate (sol)					3.0			
Sodium citrate						1.7		
Total		100.0	100.0	100.0	100.0	100.0	100.0	100.0
Concentrate								
Viscosity (cps)*								
Initial		78	270	278	337	311	83	108
14 days		71	216	248	298	310	88	103
30 days		81	228	280	457	264	88	125
90 days		85	275	910	1010	760	80	163
Aluminum Corrosion (mpy)								
70T	≤5.0	5.6	2.5	0.7	0.7	0.7	6.3	1.4
70P	≤5.0	3.3	1.6	0.6	0.5	0.6	3.7	1.1
120T	≤5.0	95.9	1.1	0.7	0.6	0.7	25.4	1.2
120P	≤5.0	58.9	1.3	0.5	0.4	0.6	12.4	0.9
Dilute Solution (5:1 mix ratio)								
Viscosity (cps)*								
Initial		1010	1090	1050	1090	1050	1050	1090
14 days		960	1040	1030	1110	1010	1010	1050
30 days		997	1040	1010	1090	396	1010	1040
90 days		960	990	1000	1050	1040	960	1000
Aluminum Corrosion (mpy)								
70T	≤2.0	9.5	1.5	0.8	0.8	0.9	1.4	0.7
70P	≤2.0	6.1	2.5	1.6	1.7	1.7	2.3	1.4
120T	≤2.0	2.5	0.8	0.7	0.7	0.8	1.2	0.6
120P	≤2.0	3.2	1.3	1.2	0.9	1.1	1.8	1.3

* Samples stored at 90°F with steel coupon suspended therein. Sample homogenized prior to measuring viscosity

The results indicate that in the absence of an iron containing corrosion inhibitor, the addition of 1.0% xanthan biopolymer has no significant effect on the corrosivity of either concentrated neat ammonium polyphosphate or its diluted solution. With reference to samples A and C, the results indicate that the addition of attapulgus clay, tolytriazole, and pigment grade iron oxide results in a dramatic reduction in the aluminum corrosivity of concentrated 11-37-0 and its diluted solutions.

With reference to samples C and D, the addition of 1.0% xanthan to 11-37-0 compositions containing attapulgus clay, tolytriazole and iron oxide further reduces the aluminum corrosivity of both the concentrated and diluted solutions. As indicated, the aluminum corrosivity of the concentrated solution is reduced to within the corrosion requirements of the specifications, but its diluted solutions, while reduced somewhat, are still marginally unacceptable.

With reference to samples E, G and I, the addition of 3.0% insoluble ferric pyrophosphate, 3.0% each of soluble and insoluble ferric pyrophosphate or a mixture of 4.3% insoluble ferric pyrophosphate, and 1.7% sodium citrate reduce the aluminum corrosivity of both the concentrated and diluted 11-37-0 solutions containing attapulgus clay and iron oxide to about the same degree as 1.0% xanthan.

With reference to samples F, H and J, the addition of 1.0% xanthan to the compositions of samples E, G and I, reduces the aluminum corrosivity of the resultant concentrate and diluted solutions to within the Forest Service Specifications in all testing conditions and situations.

The results also indicate that neat 11-37-0 ammonium polyphosphate concentrate, sample A, exhibits a viscosity of about 65 cps, while its diluted

solution has a viscosity of 5-10 cps. The addition of 1.0% xanthan biopolymer to the concentrated 11-37-0 ammonium polyphosphate solution had no significant effect on viscosity. However, upon dilution the viscosity of the resultant solution was increased initially. The viscosity of the solution gradually decreased so that it was insignificantly different than the neat solution after a relatively short period of time.

Samples M through S illustrate the impact of increasing the concentration of xanthan biopolymer from 1.0% to 3.0% in the liquid fire retardant concentrate. The data indicate that the addition of 1.0% biopolymer to an iron containing ammonium polyphosphate composition results in a further reduction in aluminum corrosivity. However, increased concentrations of xanthan biopolymer do not appear to be more effective. Additional xanthan biopolymer does appear, however, to increase the viscosity of the dilute solution to within Forest Service Specifications.

With reference to sample M, the results indicate that 3.0% xanthan biopolymer may have a slight impact on both the viscosity and aluminum corrosivity of concentrated 11-37-0 ammonium polyphosphate compositions. The diluted concentrate exhibits a stable viscosity in the range of 1000 cps, however, its aluminum corrosivity is only slightly reduced.

Samples K and R further indicate that the biopolymer has no significant impact on the viscosity of the concentrated product, but does reduce the aluminum corrosivity thereof by 50% when tested at elevated temperatures. With reference to samples L and S, the results indicate that Forest Service aluminum corrosion requirements can be met in formulations that do not include a suspending agent, such as attapulgus clay.

With reference to samples H and P, the addition of soluble ferric pyrophosphate to formulations containing insoluble ferric polyphosphate and xanthan biopolymers does not further improve aluminum corrosivity.

EXAMPLE 8-THE IMPACT OF XANTHAN BIOPOLYMERS WITH VARYING PARTICLE SIZING ON THE VISCOSITY OF LIQUID CONCENTRATE FIRE RETARDANTS

Table 8 illustrates the impact of xanthan biopolymers having various particle sizes on the rheological properties of ammonium polyphosphate fire retardant concentrates. The samples were prepared by admixing 3.0% of the xanthan biopolymers of various weight average particle size diameters, as indicated in Table 8, with concentrated ammonium polyphosphate type fire retardants. Dilution was accomplished by admixing five volumes of water with one volume of the concentrated fire retardant.

The viscosity of each dilute solution was tested by methods of testing viscosity that are well-known in the art. The rapid viscosity increase upon dilution (Diluted Viscosity – 10 minutes) was tested. The stable viscosity upon dilution (Diluted Viscosity – 30 days) was tested. The rapid viscosity increase of the solution after one-year (After 1 Year ((cps)) was tested. The stable viscosity of the solution after one-year (After 1 Year ((cps)) was tested. The results are shown below in Table 8.

TABLE 8 – PROPERTIES OF LIQUID CONCENTRATE FIRE RETARDANTS THICKENED WITH XANTHAN BIOPOLYMER WITH VARYING PARTICLE SIZING

Xanthan Biopolymer	WT. Ave. Dia (:)	Diluted Viscosity		Hydration Rate**	After 1 Year ()cps)	
		10 Minutes	30 Days		10 Minutes	30 Days
Rhodigel SM®	31	1433	1447	99	-40	-40
Jungbunzlauer ST®	38	1493	1543	98	+10	-53
Keltrol BT®	70	1147	1197	96	+126	+6
ADM 40 mesh	98	1070	1690	63	+337	+30
ADM dispersible	~105	250	1537	16	+897	+80
Kelzan® (uncoated)	110	433	547	79	NA	NA
Kelzan S® (coated)	150	120	463	26	-	-

** 10 minute viscosity as a % of maximum viscosity achieved.

The results indicate that liquid concentrate fire retardant compositions comprising biopolymers having weight average particle diameters in the range of about 31 to about 70 microns exhibit ideal rheological properties. However, fire retardant concentrates comprised of biopolymers having particle diameters larger than about 100 microns do not exhibit desirable rheological properties.

EXAMPLE 9-THE IMPACT OF PARTICLE SIZING OF THE VISCOSITY OF BIOPOLYMERS IN LIQUID CONCENTRATE FIRE RETARDANTS

Table 9 illustrates the particle sizing and performance of several xanthan-type biopolymers in comparison with standard hydroxypropyl guar gum in liquid fire retardant concentrates. The samples were prepared by admixing 3.0% xanthan type biopolymers or guar gum, as indicated below in Table 9, with concentrated ammonium polyphosphate type fire retardants. Dilution was accomplished by admixing about five volumes of water with one volume of each dilute fire retardant composition.

The viscosity of each sample ammonium polyphosphate solution was tested by the methods described in Example 8. The results are shown in Table 9 below.

TABLE 9 – IMPACT OF PARTICLE SIZING ON THE PERFORMANCE OF XANTHAN BIOPOLYMERS IN LIQUID CONCENTRATE SOLUTIONS

							ADM		
Sieve Size	Sieve Opening (microns)	Guar Gum (for comparison	Keltrol BT®	Kelzan® (uncoated)	Kelzan S® Glyoxal coated	Rhodagel SM®	40 mesh	Dispersible	Jungbunzlauer FST®
60	250		0.0	9.0	22.0	0.0	2.6	4.0	0.0
80	177		0.6	19.3	41.2	0.0	17.4	15.1	0.0
120	125		18.9	42.9	58.3	0.0	37.7	36.2	0.0
230	63		56.1	77.2	79.1	2.2	68.9	75.7	2.2
270	53		65.1	83.2	83.4	5.5	76.3	84.2	15.6
325	44		71.1	86.9	86.3	14.7	81.5	88.9	35.8
400	38		76.5	89.9	88.6	28.2	85.8	91.9	50.1
<400	<38		23.6	10.1	11.4	71.8	14.3	8.1	49.9
Particle Diameter (μ) (weight average)		>100	70	110	150	31	98	~105	38
Diluted Solution Viscosity (cps) Fresh Concentrate									
10 minutes		1597	1147	433	120	1433	1070	250	1493
30 days		63	1197	NA	463	1447	1690	1537	1543
One-Year Old Concentrate									
10 minutes		~10	1283	NA	310*	1393	1407	1147	1503
30 days		~10	1200	NA	697*	1407	1720	1617	1490

* diluted 30 days after preparation of the concentrate

The results indicate that fire retardant concentrates comprising xanthan-type biopolymers in the range of about 31 to 70 microns exhibit ideal rheological properties. However, fire retardant concentrates comprised of biopolymers having particle diameters larger than about 100 microns do not exhibit desirable rheological properties. Fire retardant concentrates comprising guar gum having a particle size diameter greater than about 100 microns also fail to exhibit desirable rheological properties. Specifically, ammonium polyphosphate based fire retardant concentrates containing guar gum appear to have highly unstable rheological characteristics, which make the use of guar gum undesirable in some embodiments of the invention. Accordingly, in one embodiment of the invention the compositions of the invention do not include guar gum.

EXAMPLE 10-THE IMPACT OF PARTICLE SIZING AND BIOPOLYMER TYPE ON THE VISCOSITY OF BIOPOLYMERS IN AMMONIUM POLYPHOSPHATE SOLUTIONS

Table 10 illustrates the particle sizing and performance of xanthan-type biopolymers with welan and rhamsan biopolymers in ammonium polyphosphate type liquid fire retardants. The samples were prepared by admixing about 91.1% concentrated liquid ammonium polyphosphate solution, 1.2% attapulgus clay, 0.3% tolytriazole, 3.0% insoluble ferric pyrophosphate and 3.0% of the biopolymer indicated in Tables 10a and 10b. The biopolymers used included Kelzan®, Kelzan S®, Keltrol BT®, Kelcorete®, and a rhamsan biopolymer, all of which are commercially available from CP Kelco, Wilmington, DE. Kelzan® is an uncoated, conventional xanthan biopolymer, while Kelzan S® is a conventional xanthan biopolymer with an applied surface coating. Keltrol BT® is a xanthan biopolymer having a particle size diameter less than about 100 microns. Kelcocrete is a welan type biopolymer.

The viscosity of each concentrate were measured by methods described in Example 8. Then, each sample was diluted with water at a mix ratio of 5 volumes of water per volume of concentrate. The 10-minute and 18-hour viscosity of the diluted sample was measured and the samples were stored in a laboratory at a temperature of about 70°F-74°F for varying periods of time, re-diluted and viscosity measured. The viscosity of each sample was measured at 10 minutes, 1 hour, 24 hours, 7 days, 15 days, 21 days and 28 days after dilution. The results are shown in Tables 10a and 10b below.

Table 10a

IMPACT OF PARTICLE SIZING AND BIOPOLYMER TYPE ON THE VISCOSITY OF AMMONIUM POLYPHOSPHATE TYPE FIRE RETARDANTS

Biopolymer		Kelzan®	Kelzan S®	Keltrol BT®	Kelcocrete®	rhamsan
Concentrate Viscosity (CPS)		196	198	189	195	199
Initial Dilution (CPS)						
	10 min.	433	140	1100	630	570
	18. hrs.	430	170	1060	1100	790
24 hrs. after Dilution						
Time after preparation	10 min.	563	173	1093	543	500
	18 hrs.	557	203	1093	1027	800
7 Days after Dilution						
	10 min.	550	98	1040	576	507
	60 min.	555	150	1057	700	620
	24 hrs.	590	187	1057	1043	840

Table 10b

IMPACT OF PARTICLE SIZING AND BIOPOLYMER TYPE ON THE VISCOSITY OF AMMONIUM POLYPHOSPHATE TYPE FIRE RETARDANTS

Biopolymer		Kelzan®	Kelzan S®	Keltrol BT®	Kelcocrete®	rhamsan
Concentrate Viscosity (CPS)		196	198	189	195	199
15 Days after Dilution						
	10 min.	490	160	1047	440	467
	60 min.	503	177	1077	617	550
	24 hrs.	540	217	1103	1010	823
21 Days after Dilution						
	10 min.	710	243	1083	410	550
	60 min.	747	247	1107	570	663
	24 hrs.	687	397	1043	937	837
28 Days after Dilution						
	10 min.	547	200	1043	937	837
	60 min.	563	237	1063	650	710
	24 hrs.	613	260	1057	1047	903

The results indicate that welan and rhamsan type biopolymers thicken more slowly than xanthan type biopolymers but are effective at increasing the viscosity of ammonium polyphosphate type fire retardant solutions. Xanthan type biopolymers having a particle size diameter of less than about 100 microns, however, rapidly increase the viscosity of ammonium polyphosphate type fire retardants upon dilution. Conventional biopolymers, e.g. xanthan type biopolymers having particle size diameters greater than about 100 microns, fail to develop the viscosity of the fire retardants in a timely manner. Accordingly, both coated and uncoated conventional biopolymers are unsuitable for use in thickening ammonium polyphosphate type fire retardants. In addition, the long-term data, i.e. measured viscosity 7, 15, 21 and 28 days after preparation of the concentrated sample, indicate that there is no particular change in the performance of the various biopolymers during storage in ammonium polyphosphate based fire retardants.

EXAMPLE 11- IMPACT OF USE LEVELS OF BIOPOLYMERS AND IRON ADDITIVES ON THE VISCOSITY OF AMMONIUM POLYPHOSPHATE SOLUTIONS

The optimal use levels of mixtures of biopolymer and insoluble ferric pyrophosphate when used to reduce the aluminum corrosion level of liquid ammonium polyphosphate type fire retardants and their dilute solutions was analyzed. Formulations were prepared by using ammonium polyphosphate type fire retardants with attapulgus clay, tolytriazole, and in some cases, iron oxide. Biopolymers having average particle size diameters of less than 100 microns and insoluble ferric pyrophosphate were also added, where indicated. Each formulation was prepared by adding the dry components separately to the fire retardants and mixing them using a high shear mixer at approximately 1000 rpm

over about a 2 hour period. The high shear was used to hydrate the clay and disperse the insoluble components. Dilute solutions were prepared by admixing 1 part concentrate with 5 parts tap water. The concentrate formulations and their dilute solutions were tested in accordance with all four of the test conditions prescribed by the U.S. Forest Service Specifications, described herein. The results are shown below in Tables 11a, 11b and 11c.

Table 11a

Formulation Components (wt. %)	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
Ammonium Polyphosphate	100.0	93.10	96.80	95.80	94.80	96.55	95.55	94.55	96.30	95.30	94.30	96.50	95.50	96.25	95.25
Attapulgus clay	-	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40
Tolyltriazole	-	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30
Iron Oxide (Red)	-	1.20	-	-	-	-	-	-	-	-	-	-	-	-	-
Iron Oxide (Brown)	-	-	-	-	-	-	-	-	-	-	-	0.30	0.30	0.30	0.30
Keltrol BT	-	1.00	0.50	0.50	0.50	0.75	0.75	0.75	1.00	1.00	1.00	0.50	0.50	0.75	0.75
Ferric Pyrophosphate (Insol.)	-	3.00	1.00	2.00	3.00	1.00	2.00	3.00	1.00	2.00	3.00	1.00	2.00	1.00	2.00
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Concentrate															
Viscosity (cps)*															
Initial	61	193	148	161	157	150	145	160	150	166	167	168	156	161	173
14 days	57	421	363	173	218	365	256	198	193	208	187	210	168	175	220
30 days	70	430	390	205	230	390	433	285	273	325	373	305	418	308	345
90 days	61	1850	1940	750	1150	1010	1360	1310	1010	860	1390	900	1430	1000	1050
Aluminum Corrosion (mpy)															
70T ≤5.0	4.8	0.4	3.6	0.9	0.6	3.8	1.0	0.6	3.6	1.3	0.9	2.9	1.2	2.7	1.0
70P ≤5.0	2.6	0.5	1.7	0.6	0.5	2.0	0.8	0.5	1.9	0.9	0.7	1.6	0.7	1.4	0.7
120T ≤5.0	112.4	0.7	18.9	1.2	1.0	15.2	1.1	0.9	11.9	1.5	1.1	7.1	1.2	5.3	0.9
120P ≤5.0	69.4	0.5	43.9	0.8	0.6	16.2	0.9	0.6	46.4	0.9	0.8	3.7	0.7	2.8	0.5
Dilute solution (5:1 mix ratio)															
Refractive Index	14.5	14.5	14.6	15.0	15.4	15.4	15.4	15.3	15.0	15.6	15.4	15.0	14.9	15.0	15.0
Viscosity (cps)*															
Initial	5	146	50	50	53	105	98	100	153	172	159	53	52	109	103
14 days	5	130	30	43	40	85	78	85	138	155	143	50	45	91	97
30 days	5	132	31	37	33	90	80	84	125	145	126	33	61	73	79
90 days	5	90	18	13	19	23	43	23	28	70	40	15	15	23	29
Aluminum Corrosion (mpy)															
70T ≤2.0	11.3	0.7	1.3	1.0	1.0	1.4	1.1	0.8	1.2	0.8	0.8	1.2	1.3	1.5	1.0
70P ≤2.0	6.8	1.9	3.9	3.1	3.0	3.5	3.3	2.9	3.6	2.9	2.4	3.2	3.1	3.3	2.8
120T ≤2.0	5.1	0.8	0.9	0.6	0.6	0.8	0.7	0.4	0.7	0.5	0.7	1.2	1.3	0.7	0.5
120P ≤2.0	5.8	1.5	1.7	2.3	2.2	1.8	2.5	1.6	2.4	1.7	1.2	1.9	2.6	2.1	2.0

*Samples stored at 90°F with steel coupon suspended therein. Samples homogenized prior to measuring viscosity.

Table 11b

Comparison of 0.5, 0.75, and 1.0% Keltrol BT														
Formulation Components (wt. %)	C	F	I	L	N	D	G	J	M	O	B	E	H	K
Ammonium Polyphosphate	96.80	96.55	96.30	96.50	96.25	95.80	95.55	95.30	95.50	95.25	93.1	94.80	94.55	94.30
Attapulgus clay	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.4	1.40	1.40	1.40
Tolyltriazole	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.3	0.30	0.30	0.30
Iron Oxide (Red)	-	-	-	-	-	-	-	-	-	-	1.2	-	-	-
Iron Oxide (Brown)	-	-	-	0.30	0.30	-	-	-	0.30	0.30	-	-	-	-
Keltrol BT	0.50	0.75	1.00	0.50	0.75	0.50	0.75	1.00	0.50	0.75	1.00	0.50	0.75	1.00
Ferric Pyrophosphate (Insol.)	1.00	1.00	1.00	1.00	1.00	2.00	2.00	2.00	2.00	2.00	3.00	3.00	3.00	3.00
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Concentrate														
Viscosity (cps)*														
Initial	148	150	150	168	161	161	145	166	156	173	193	157	160	167
14 days	363	365	193	210	175	173	256	208	168	220	421	218	198	187
30 days	390	390	273	305	308	205	433	325	418	345	430	230	285	373
90 days	1940	1010	1010	900	1000	750	1360	860	1430	1050	1850	1150	1310	1390
Aluminum Corrosion (mpy)														
70T ≤5.0	3.6	3.8	3.6	2.9	2.7	0.9	1.0	1.3	1.2	1.0	0.4	0.6	0.6	0.9
70P ≤5.0	1.7	2.0	1.9	1.6	1.4	0.6	0.8	0.9	0.7	0.7	0.5	0.5	0.5	0.7
120T ≤5.0	18.9	15.2	11.9	7.1	5.3	1.2	1.1	1.5	1.2	0.9	0.7	1.0	0.9	1.1
120P ≤5.0	43.9	16.2	46.4	3.7	2.8	0.8	0.9	0.9	0.7	0.5	0.5	0.6	0.6	0.8
Dilute solution (5:1 mix ratio)														
Refractive Index	14.6	15.4	15.0	15.0	15.0	15.0	15.4	15.6	14.9	15.0	14.5	15.4	15.3	15.4
Viscosity (cps)*														
Initial	50	105	153	53	109	50	98	172	52	103	146	53	100	159
14 days	30	85	138	50	91	43	78	155	45	97	130	40	85	143
30 days	31	90	125	33	73	37	80	145	61	79	132	33	84	126
90 days	18	23	28	15	23	13	43	70	15	29	90	19	23	40
Aluminum Corrosion (mpy)														
70T ≤2.0	1.3	1.4	1.2	1.2	1.5	1.0	1.1	0.8	1.3	1.0	0.7	1.0	0.8	0.8
70P ≤2.0	3.9	3.5	3.6	3.2	3.3	3.1	3.3	2.9	3.1	2.8	1.9	3.0	2.9	2.4
120T ≤2.0	0.9	0.8	0.7	1.2	0.7	0.6	0.7	0.5	1.3	0.5	0.8	0.6	0.4	0.7
120P ≤2.0	1.7	1.8	2.4	1.9	2.1	2.3	2.5	1.7	2.6	2.0	1.5	2.2	1.6	1.2

*Samples stored at 90°F with steel coupon suspended therein. Samples homogenized prior to measuring viscosity.

Table 11c

Comparison of 1.0, 2.0, 3.0% Insoluble Ferric Pyrophosphate														
Formulation Components (wt. %)	C	D	E	L	M	F	G	H	N	O	B	I	J	K
Ammonium Polyphosphate	96.80	95.80	94.80	96.50	95.50	96.55	95.55	94.55	96.25	95.25	93.1	96.30	95.30	94.30
Attapulgus clay	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.4	1.40	1.40	1.40
Tolyltriazole	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.3	0.30	0.30	0.30
Iron Oxide (Red)	-	-	-	-	-	-	-	-	-	-	1.2	-	-	-
Iron Oxide (Brown)	-	-	-	0.30	0.30	-	-	-	0.30	0.30	-	-	-	-
Keltrol BT	0.50	0.50	0.50	0.50	0.50	0.75	0.75	0.75	0.75	0.75	1.00	1.00	1.00	1.00
Ferric Pyrophosphate (Insol.)	1.00	2.00	3.00	1.00	2.00	1.00	2.00	3.00	1.00	2.00	3.00	1.00	2.00	3.00
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Concentrate														
Viscosity (cps)*														
Initial	148	161	157	168	156	150	145	160	161	173	193	150	166	167
14 days	363	173	218	210	168	365	256	198	175	220	421	193	208	187
30 days	390	205	230	305	418	390	433	285	308	345	430	273	325	373
90 days	1940	750	1150	900	1430	1010	1360	1310	1000	1050	1850	1010	860	1390
Aluminum Corrosion (mpy)														
70T ≤5.0	3.6	0.9	0.6	2.9	1.2	3.8	1.0	0.6	2.7	1.0	0.4	3.6	1.3	0.9
70P ≤5.0	1.7	0.6	0.5	1.6	0.7	2.0	0.8	0.5	1.4	0.7	0.5	1.9	0.9	0.7
120T ≤5.0	18.9	1.2	1.0	7.1	1.2	15.2	1.1	0.9	5.3	0.9	0.7	11.9	1.5	1.1
120P ≤5.0	43.9	0.8	0.6	3.7	0.7	16.2	0.9	0.6	2.8	0.5	0.5	46.4	0.9	0.8
Dilute solution (5:1 mix ratio)														
Refractive Index	14.6	15.0	15.4	15.0	14.9	15.4	15.4	15.3	15.0	15.0	14.5	15.0	15.6	15.4
Viscosity (cps)*														
Initial	50	50	53	53	52	105	98	100	109	103	146	153	172	159
14 days	30	43	40	50	45	85	78	85	91	97	130	138	155	143
30 days	31	37	33	33	61	90	80	84	73	79	132	125	145	126
90 days	18	13	19	15	15	23	43	23	23	29	90	28	70	40
Aluminum Corrosion (mpy)														
70T ≤2.0	1.3	1.0	1.0	1.2	1.3	1.4	1.1	0.8	1.5	1.0	0.7	1.2	0.8	0.8
70P ≤2.0	3.9	3.1	3.0	3.2	3.1	3.5	3.3	2.9	3.3	2.8	1.9	3.6	2.9	2.4
120T ≤2.0	0.9	0.6	0.6	1.2	1.3	0.8	0.7	0.4	0.7	0.5	0.8	0.7	0.5	0.7
120P ≤2.0	1.7	2.3	2.2	1.9	2.6	1.8	2.5	1.6	2.1	2.0	1.5	2.4	1.7	1.2

*Samples stored at 90°F with steel coupon suspended therein. Samples homogenized prior to measuring viscosity.

The results indicate that the incorporation of some iron oxide within fire retardant concentrates and solutions of the present inventions is necessary to meet U.S. Forest Service Specification requirements. Fire retardant concentrates that include 1.2% iron oxide, 3% ferric pyrophosphate and 1% biopolymer, and their diluted solutions meet the U.S. Forest Service Specification requirements. The viscosity of the fire retardant concentrates containing 1% biopolymer gradually increased from about 150 to 200 cps immediately after manufacture to 1000 to 2000 cps. After three months of storage at 90°F, and upon dilution, the solution viscosity was in the range of 100 to 200 cps.

In view of the above, it is seen that the various objects and features of the invention are achieved and other advantages and results are obtained. Variations and modification may be made to the various steps and compositions of the invention without departing from the scope of the invention.